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CHEMOTAXONOMY OF DICTYOTALES (PHAEOPHYTA). 2. THE "*DICTYOTA*" GROUP. (*)

QUIMIOTAXONOMIA DE DICTYOTALES (PHAEOPHYTA). 2. O GRUPO "*DICTYOTA*". (*)

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RESUMO

O grupo "*Dictyota*" de algas tem apresentado mais de 180 diterpenos de 27 tipos diferentes de esqueletos. Foram isolados de 28 espécies pertencentes ao gênero Dictyota (16 espécies), Dilophus (6), Glossophora(2), Pachydictyon(1), Spatoglossum(2) e Stoechospermum (1). Os diterpenos tem sido separados em três grupos químicos (I a III), dependendo da primeira ciclização do precursor biossintético, o geranil-geraniol. Metabólitos tem sido caracterizados por índices de oxidação e de esqueleto. As médias dos valores desses índices, calculadas para cada grupo químico (I a III), em cada gênero considerado, indicam que os diterpenos são bons marcadores taxonômicos para o grupo "*Dictyota*".

PALAVRA CHAVE: diterpenos , Dictyotaceae, grupo "*Dictyota*".

ABSTRACT

The "*Dictyota*" group of algae has furnished more than 180 diterpenes, with 27 different skeleton types. They have been isolated from 28 species that belong to the genera Dictyota (16 species), Dilophus

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* Previous paper in this series, see TEIXEIRA and KELECOM (1987b).

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(6), Glossophora (2), Pachydictyon (1), Spatoglossum (2) and Stoechospermum (1). Diterpenes have been separated into three chemical groups (I to III) depending on the first formal cyclization of their common biosynthetic precursor, geranyl-geraniol. Metabolites have been characterized by oxidation and skeleton indices. The mean values of these indices, calculated for each chemical group (I to III) in each considered genus indicated that diterpenes are valuable taxonomic markers of the "*Dictyota*" group.

KEY WORDS: diterpenes, Dictyotaceae, "*Dictyota*" group.

INTRODUCTION

The representatives of the order Dictyotales have emerged as an exceptionally rich source of bioactive substances, which seem to take part, in the marine environment, of a defensive strategy against predation by herbivores (FENICAL 1980, KELECOM AND TEIXEIRA 1986). According to PAPENFUSS (1977), the order Dictyotales is composed of one single family, Dictyotaceae. that includes 16 tropical and subtropical genera distributed all over the world. Chemical investigation on nine of these genera have resulted in the isolation of a large array of secondary metabolites, the nature of which allowed to separate Dictyotaceae into three groups refered to as the "Dictyopteris", "Taonia" and "Dictyota" groups (FENICAL 1980).

The "Dictyopteris" group includes species of the genus *Dictyopteris*. These algae produce mainly odoriferous hydrocarbons, sulfur-containing metabolites and sesquiterpenes thet may be or not from mixed biosynthetic origin.

The "*Taonia*" group is composed of two genera, and *Stypopodium*, both producing terpenes of mixed biosynthetic origin, some of which seem to be closely related to metabolites from the order Fucales (FENICAL 1978).

Finally, the "Dictyota" group gathers morphologically similar plants that belong to the genera *Dictyota, Dilophus, Glossophora, Pachydictyon, Spatoglossum* and *Stoechospermum*. All these algae produce diterpenes whose skeletons are almost exclusively found in marine organisms (TEIXEIRA et alii 1985).

In a previous study, we showed that the geographic distribution of the diterpenes from the genus *Dictyota* parallels the biogeography of the taxon (TEIXEIRA AND KELECOM 1987 a). We also showed that the diterpenes from Dictyota species appear to be valuable taxonomic markers and that they showed, for several species, strong correlation with botanic data (TEIXEIRA AND KELECOM 1987 b).

The present work analyses diterpenes as potential taxonomic markers in the group "Dictyota", For this aim, the semi-empiric techniques described by O.R. GOTTLIEB (1982) have been extensivelly used and have been compared with literature data on morphologic aspects and on geographic distribution (HENRIQUEZ 1982).

RESULTS

Chemical data are available for 28 species of the "Dictyota" group of which 16 belong to the genus *Dictyota* (ALVARADO AND GERMICK 1985, AMICO et alii 1980, 1981, BLOUNT et alii 1982, CLARDY et alii 1987, CREWS et alii 1982, DANISE et alii 1977, DEMATTE et alii 1985a, 1985b, DE ROSA et alii 1986, ENOKI et alii 1982a, 1982b, 1983a, 1983b, 1983c, 1984, 1985, FAULKNER et alii 1977, FATTORUSSO 1977, FATORUSSO et alii 1976, FINNER et alii 1979, GONZALEZ et alii 1982, 1983, 1984, 1987, KATO et alii 1987, KIRKUP AND MOORE 1983a, 1983b KUSUMI et alii 1986a, 1986b, NIANG AND HUNG 1984, OCHI et alii 1980a, 1980b, 1981, 1986, PATHIRANA AND ANDERSEN 1984, PEREZ et alii 1987, PULLAIAH et alii 1985, RAO et alii 1986, ROBERTSON AND FENICAL 1977, SCHNETTER et alii 1987, SEGAWA et alii 1987, SUN AND FENICAL 1979a, SUN et alii 1977, 1981, 1983, TANAKA AND HIGA 1984, TEIXEIRA et alii 1986a, 1986b, TRINGALI et alii 1986a), 6 to the genus *Dilophus* (AMICO et alii 1976, 1977, 1979, DE ROSA et alii 1984, KASLAUSKAS et alii 1978, KURATA et alii 1988, OCHI et alii 1982, RAVI AND WELLS 1982a, 1982b, SCHLENK AND GERWICK 1987, TRINGALI et alii 1984a, 1984b, 1984c, 1985, 1986b), 2 to the genus *Glossophora* RIVERA et alii 1987, SUN AND FENICAL 1979b), 1 to the genus *Pachydictyon* (HIRSCHFELD et alii 1973, ISHITSUKA et alii 1982, 1983a, 1983b, 1984a, 1984b, 1986), 2 to the genus *Spatoglossum* (GERWICK et alii 1980, GERWICK AND FENICAL 1983) and 1 to the genus *Stoechospermum* (DE SILVA et alii 1982, GERWICK et alii 1981, RAO et alii 1987, SOLIMABI et alii 1980). More Than 180 diterpenes, distributed in 27 different carbon skeletal classes, have been isolated until July 1988 from the here refered species (see Table 1). All diterpenes were divided into three biogenetic groups accorging to previous considerations on the first formal cyclization of the geranyl-geraniol precursos (TEIXEIRA et alii 1985, TEIXEIRA AND KELECOM 1987b).

Diterpenes of group I (Figure 1) result from a first cyclization between positions 1 and 10 or 1,10 and 1,11 of geranyl-geraniol. Such diterpenes are mainly isoprenologues of well known sesquiterpenes skeletons. Diterpenes of group II (Figure 2) are originated from cyclization of the acyclic precursor between C-1 C-11, meanwhile diterpenes of group III (Figure 3) seem to derive from an anti-Markovnikov cyclization of geranyl-geraniol between positions 2 and 10. However, following ENOKI and coworkers (1985), diterpenes of the xeniane group (group III) should derive from ring contraction of a germacrane-type (group I) precursor, and this hypothesis has received some support from chemotaxonomic considerations (TEIXEIRA AND KELECOM 1987b).

According to GOTTLIEB (1982), the specialization index (SI) has been calculated for each skeleton, and the skeletal evolutive advancement index (IAs) was obtained as the arithmetic mean of the SI values of all skeletons that occur in a specific genus. Each diterpene described was characterized by its oxidation index (OI), and each genus by a mean oxidation index (IAo) that was calculated as the arithmetic mean of the OI values of all diterpenes isolated from the genus.

Table 1 shows all studied species, the number of diterpenes isolated from each genus and their skeletal types.

The genus Dictyota, with 16 species studied and 115 identified diterpenes, is the most diversified as far as skeletons are concerned. These belong to the three chemical groups: six skeletons to group I, seven to group II and six to group III. The latter group is almost exclusively found in species from the Pacific Øcean. Each species of *Dictyota* produces diterpenes whose skeletons belong either esclusively to groups I or II, or to groups I and III. With the excepcion of *D. dichotoma*, no *Dictyota* species produced diterpenes that belong exclusively to group III, neither to group II together with groups I or III (TEIXEIRA AND KELECOM 1987b).

The genus *Dilophus*, with six species studied and 48 diterpenes reported, is rich in metabolites with skeletons of group I (a total of 5). Groups II and III were represented by only two skeletons each. These skeletons are respectively characteristic of the Mediterranean Sea (dolabellane) and of the Pacific Ocean (xeniane). Finally, this genus is also the only one that produced an acyclic diterpene.

The genus *Glossophora*, studied for two species of the Galapagos

Islands and of the Chilean coast, possesses diterpenes with skeletons of groups I and II (prenylated guaiane and dolabellane, respectively), and this is contrastant with our results on the genus *Dictyota* (TEIXEIRA AND KELECOM 1987b) (see above), and also highly unusual in representants of the group "Dictyota".

The genus *Pachydictyon*, restricted to the Pacific Ocean, yielded twenty four diterpenes that belong to the three skeletal groups (I, II and III). The latter group, represented by five skeletons, is structurally the most diversified one.

The genera *Spatoglossum* and *Stoechospermum*, with respectively two and one studied species, afforded only one skeleton type (spatane) that belong to group I.

Thus, the "Dictyota" group produced in 29 species, 185 diterpenes distributed as such: 10 skeletons in group I, 8 in group II and 8 in group III. Figure 4 represents, for each genus, the pertent distributions of the diterpenes, considering their biogenetic origin (groups I, II and III).

Diterpenes from *Dictyota* species are unequally distributed in three chemical groups: 28% belong to group I, 46% to group II and 26% to group III. In the genus *Dilophus* 52% of the diterpenes belong to group I, 29% to group II, 17% to group III and 2% (1 structure) is an acyclic diterpene. The genus *Glossophora* produces diterpenes from group I (67%) and II (33%). *Pachydictyon* furnished diterpenes from groups I (29%), II (4%) and III (67%). The genera *Spatoglossum* and *Stoechospermum* yilded 100% diterpenes having the spatane skeleton (group I).

In Figure 5, the indice of evolutive advancement of the skeletons (IAs) are plotted against the mean oxidation indices (IAo) for each genus of the "Dictyota" group, considered as a whole (M) or split into the three chemical groups (I, II and III).

Among the diterpenes of group I, the highest values as IAs and IAo were observed for the genera *Stoechospermum* (0.15 and -1.25), *Spatoglossum* (0.15 and -1.26) and *Dilophus* (0.15 and -1.27). The genus *Pachydictyon* had the lowest IAs value for metabolites of group I (0.07) and also a low IAo value (-1.42). Considering diterpenes of group II, the highest IAs value was observed in *Dictyota* (0.14) and the highest IAo values were found in *Dilophus* (-1.27) and *Dictyota* (-1.31).

In all genera, diterpenes of group III had low IAs value (0.06 to 0.09), but showed, in *Dilophus*, the most oxidized diterpenes (-1.05). Indeed, the genus *Dilophus* produced, for each chemical

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In all genera, diterpenes of group III had low IAs values (0.06 to 0.09), but showed, in *Dilophus*, the most oxidized diterpenes (-1.05). Indeed, the genus *Dilophus* produced, for each chemical group, diterpenes more oxidized than did the other genera.

The genus *Dictyota*, produce diterpenes of the three groups. It was characterized by the presence of metabolites from group II that were both structurally diversified (7 skeletons) and that dominated in number (45%) the diterpenes of this genus. Compounds had high specialization index (0.14), and were reasonably oxidized (-1.31).

The genus *Dilophus* furnished diterpenes of the three groups, and was characteristic for the presence of highly oxidized diterpenes (group I : IAo = -1.27; group II : IAo = -1.27 and group III : IAo = -1.05). Compounds from Group I had high IAs value (0.15) and dominated numerically the genus (52%).

The genus *Glossophora* had diterpenes of groups I and II that had low specialization (IAs = 0.10) and oxidation levels (group I: IAo = -1.31 and Group II: IAo = - 1.49).

The genus *Pachydictyon* produced diterpenes from the three groups. Diterpenes of groups I and II were characterized by low oxidation and skeleton indices (I : IAo = -1.42, IAs = 0.07; II : IAo = -1.60, IAs = 0.10). Diterpenes of group III are more oxidized (IAo = -1.26) but are not very evoluted (IAs = 0.08).

The genera *Spatoglossum* and *Stoechospermum*, with diterpenes restricted to group I, showed high specialization and oxidation indices (IAs = 0.15 for both genera; IAo = -1.26 and -1.25 for *Spatoglossum* and *Stoechospermum* respectively).

On the whole, the highest mean values for IAs and IAo were observed in *Spatoglossum* (0.15 and -1.26), *Stoechospermum* (0.15 and -1.25) and *Dilophus* (0.15 and -1.24). On the contrary, the lowest values were observed for *Glossophora* (0.10 and -1.37) and *Pachydictyon* (0.08 and -1.32). The most studied genus *Dictyota* showed intermediate values for both indices (0.11 and -1.32).

DISCUSSION

Diterpenes are useful taxonomic markers of the"Dictyota" group. The skeletal evolutive advancement index (IAs) and the oxidation index (IAo) are different and characteristic for about all the genera we studied. The indexes showed direct correlation between the dominant character of a particular skeleton (group I, II or III) and the degree of specialization of isolated diterpenes. Thus, the genus *Dictyota* produces mainly skeletons of group II (more particularly dolabellanes and dolastanes) which had high specialization (IAs = 0.14) and oxidation (IAo = -1.31) indexes.The genus *Dilophus* is characterized by the presence of highly oxidized diterpenes in the three chemical groups and by the dominant presence of terpenes from group I (principally seco-spatanes) they were rather oxidized (IAo = -1.27) and specialized (IAs = 0.15).

The genus *Pachydictyon* had unspecialized and low oxidized diterpenes. When compared with the other genera, the oxidation level was higher only in diterpenes of group III (-1.26) that also dominate in this genus. *Glossophora* is unique in having diterpenes of groups I and II. In *G. galapagensis*, these are neither highly specialized nor oxidized. This originality may be related to the geographic isolation of the Galapagos Islands where considered species had been collected, isolation that led to an original fauna and that may have led, microscopically, to a different diterpene pattern. The genera *Spatoglossum* and *Stoechospermum* are at present chemically undistinguishable and produced highly oxidized and specialized diterpenes of the single spatane skeleton.

The dominance of one biosynthetic way leading to diterpenes of groups I, II or III may be closely related, in the "Dictyota" group, to predation pressure and to geographic remoteness of the species from their dispertion centrum (TEIXEIRA AND KELECOM 1987a). If this assumption is true, group I diterpenes, that are found in species collected in all the oceans, seen to be efficient defense mechanism for the genera *Dilophus*, *Spatoglossum* and *Stoechospermum*. On the other hand, diterpenes of group II should then be the most efficient anti-herbivory substances of Dictyota, more particularly dolabellanes in the Mediterranean Sea and in the Indian Ocean, dolastanes in the Atlantic Ocean and xenianes together with dolastanes in the Pacific Ocean.

Pachydictyon coriaceum, restricted to the Pacific Ocean where Dictyotales possibly originated (CHAPMAN AND CHAPMAN 1981), has more simple and reduced diterpenes. The biosynthetic way leading to group III seem to be effective for herbivory control only in the Pacific area.

Finally, it should be noted that the genus *Dilophus*, although morphologically similar to algae of the group "Dictyota", possesses an heterogenous chemical composition. Indeed, when the majority of *Dilophus* species produces diterpenes, *Dilophus fasciola* yields sesqui-and diterpenes. The taxonomic position of this genus, based on chemical criterions, is still not well defined.

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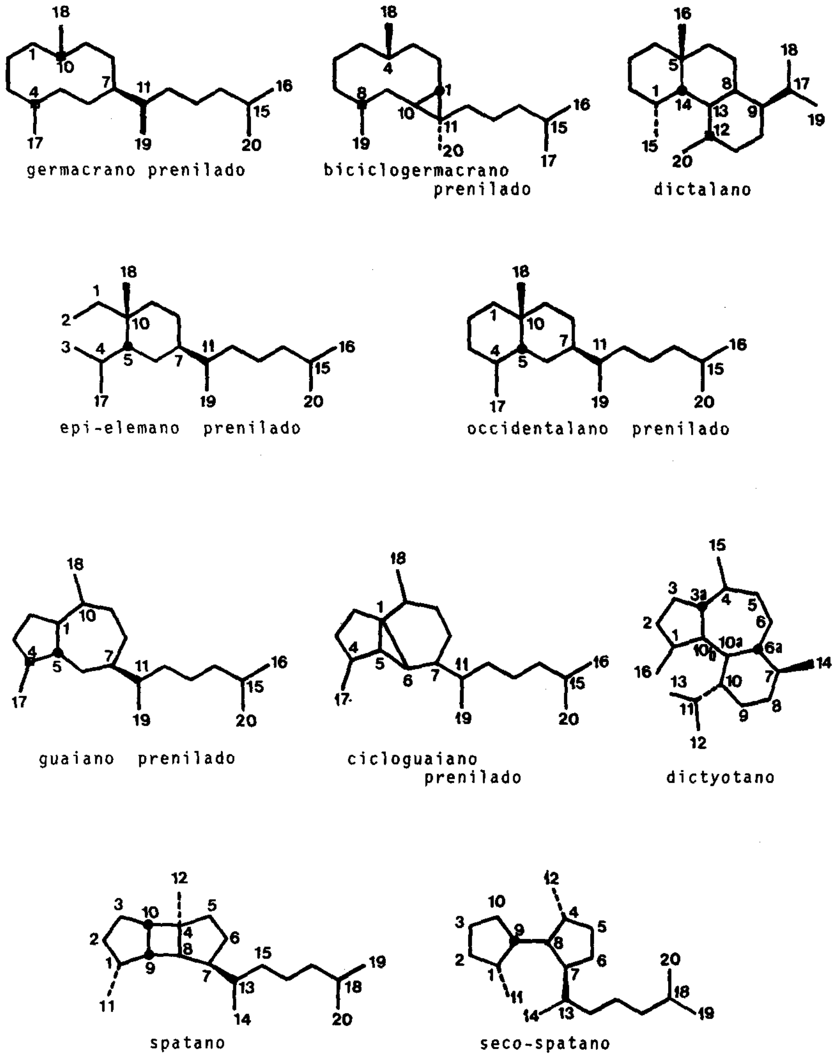


Figure 1 : *diterpene skeletons of* Group-I

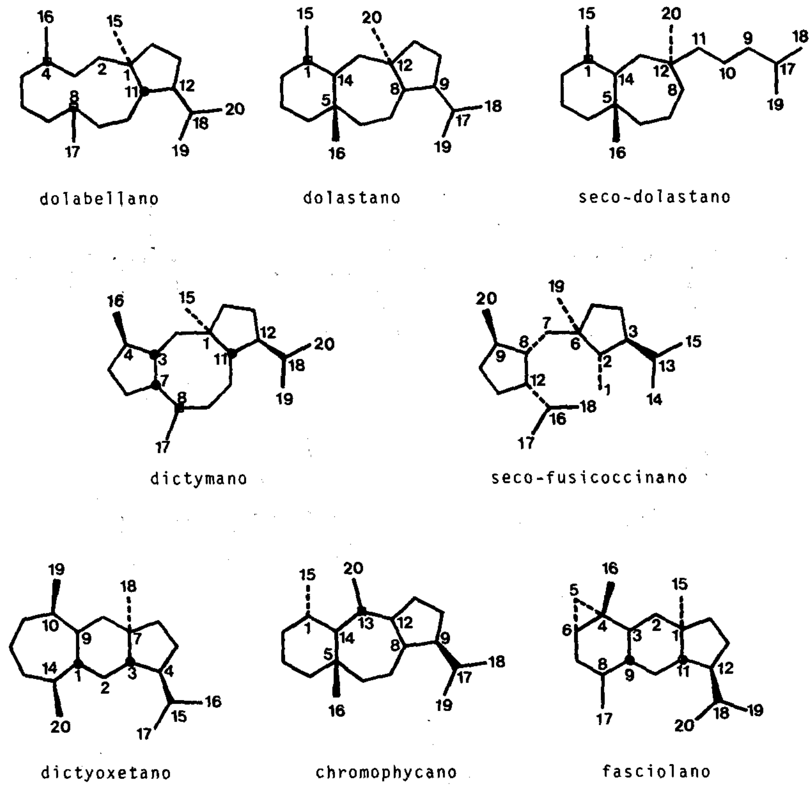
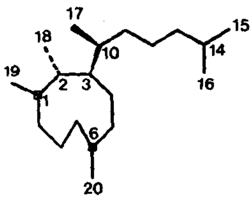
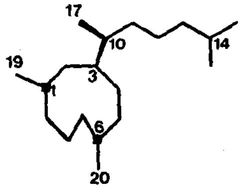


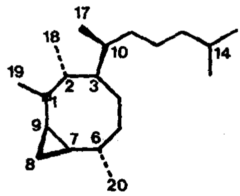
Figure 2 : *diterpene skeletons of* Group-II



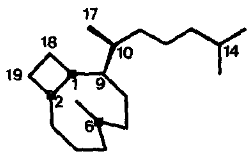
xeniano



18-*nor*-xeniano



crenulidano



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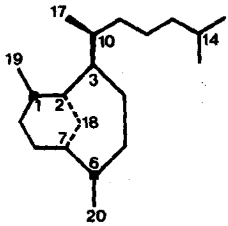
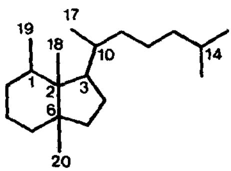


crenulano



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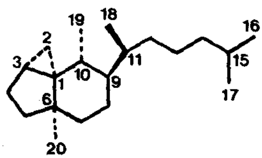
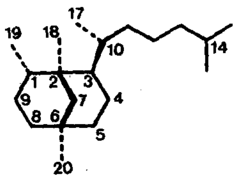


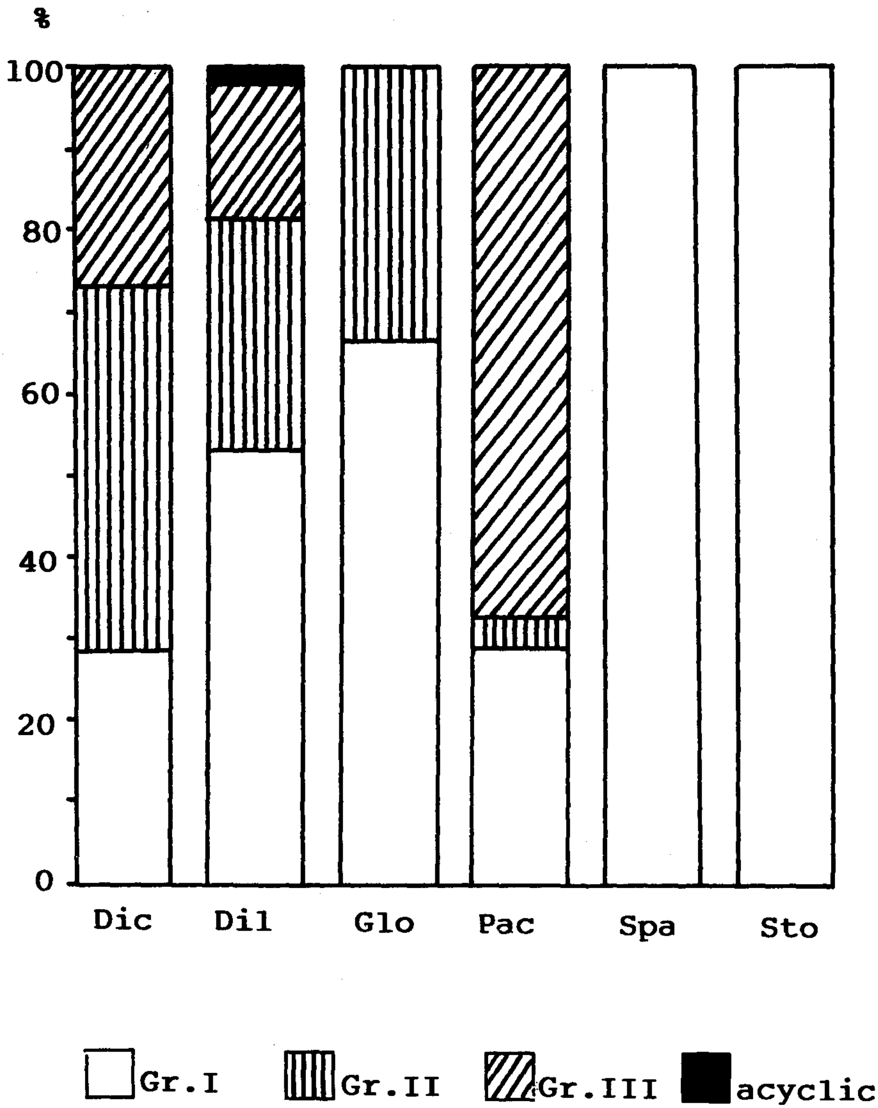
triciclodictyotano



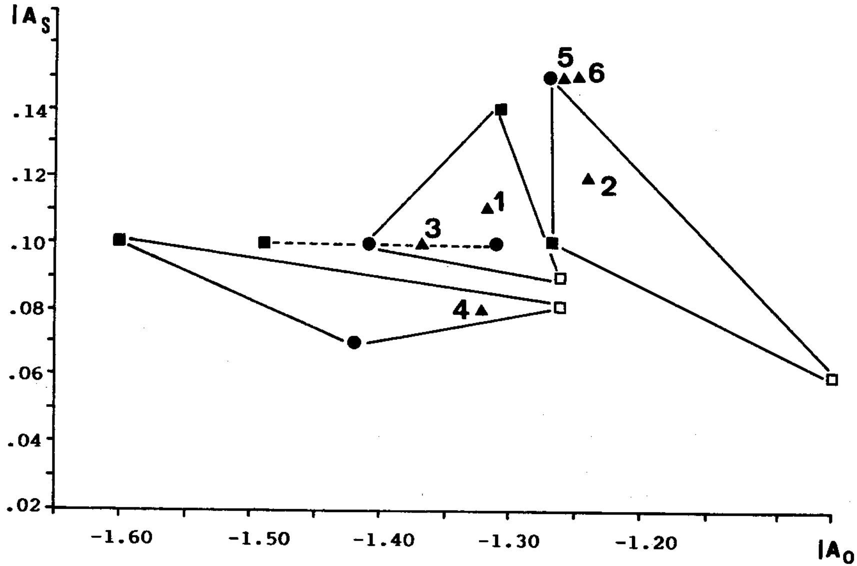
dichotomano

Figure 3 : *diterpene skeletons of* Group-III

Diterpenes from the "Dictyota" group :
% distribution



$|A_o \times |A_s$: diterpenes from the "Dictyota" group



● Group I ■ Group II □ Group III ▲ mean

1 : Dictyota ; **2** : Dilophus ; **3** : Glossophora ;
4 : Pachydictyon ; **5** : Spatoglossum ; **6** : Stoechospermum

DITERPENE SKELETONS (Number of structures)

Genera	Number of species	Group I	Group II	Group III	Total
Dictyota	16	dictalane (02) dictyotane (01) epi-elemane pren. (01) germacrane pren. (04) guaiane pren. (24) occidentalane pren. (01) **Total**: 33	chromophycane (01) dictymane (01) dictyoxetane (01) dolabellane (23) dolastane (21) secodolastane (04) secofusicoccinane (01) **Total**: **52**	cycloxeniane (02) crenulane (02) crenulidane (06) dichotomane (02) tricyclodictyotane (03) xeniane (15) **Total**: **30**	115
Dilophus	6	bicyclogermacrane pren. (04) cycloguaiane pren. (03) germacrane pren. (01) secospatane (09) spatane (06) **Total**: **26**	dolabellane (13) fasciolane (01) **Total**: 14	crenulane (01) xeniane (07) **Total**: 8	48*
Glossophora	2	guaiane pren. (06) **Total**: 6	dolabellane (03) **Total**: 3		9
Pachydictyon	1	germacrane pren. (04) guaiane pren. (03) Total: 7	dolabellane (01) Total: 1	coriacenane (02) crenulane (02) crenulidane (03) nor-xeniane (01) xeniane (08) **Total**: **16**	24
Spatoglossum	2	spatane (05) Total: **5**			5
Stoechospermum	1	spatane (11) Total: **11**			11
T O T A L	28	10 skeletons (76 terpenes)	8 skeletons (66 terp.)	8 skeletons (42 terpenes)	185

* acyclic diterpene also present

TABLE 1 - Number of species studied, skeletons and diterpenes isolated from each genus.